

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
20 September 2001 (20.09.2001)

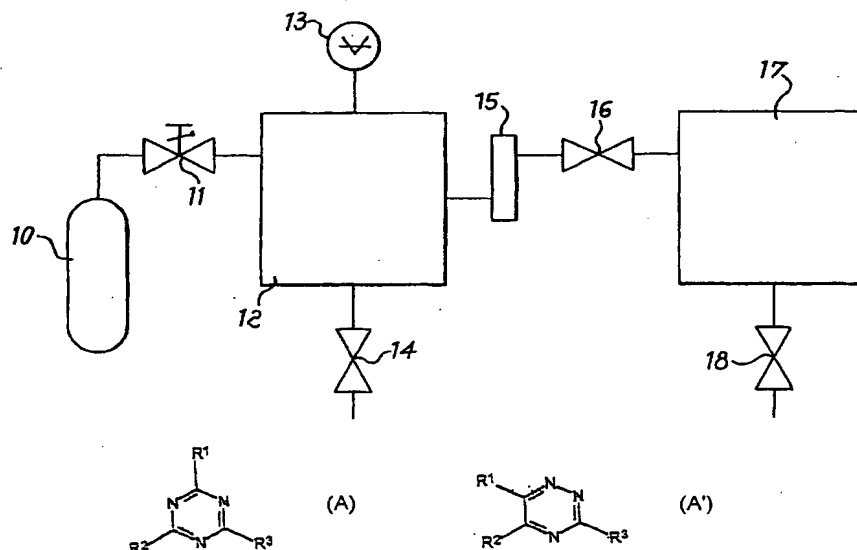
PCT

(10) International Publication Number  
**WO 01/68516 A1**(51) International Patent Classification<sup>7</sup>: **C01B 3/00,**  
**C07D 253/06, 251/30**(21) International Application Number: **PCT/IT01/00105**(22) International Filing Date: **2 March 2001 (02.03.2001)**(25) Filing Language: **English**(26) Publication Language: **English**(30) Priority Data:  
**MI2000A000529 15 March 2000 (15.03.2000) IT**(71) Applicant (for all designated States except US): **SAES**  
**GETTERS S.P.A. [IT/IT]; Viale Italia, 77, I-20020 Lainate**  
**(IT).**

(72) Inventors; and

(75) Inventors/Applicants (for US only): **MONTANARI,**  
**Fernando [IT/IT]; Università di Milano, Dip. Chimica**  
**Organica e Industriale, Via Golgi, 19, I-20100 Milano**  
**(IT). QUICI, Silvio [IT/IT]; Università di Milano, Dip.**Chimica Organica e Industriale, Via Golgi, 19, I-20100  
Milano (IT). **MANFREDI, Amedea [IT/IT];** Università  
di Milano, Dip. Chimica Organica e Industriale, Via  
Golgi, 19, I-20100 Milano (IT). **VILLA, Elena [IT/IT];**  
Università di Milano, Dip. Chimica Organica e Industriale,  
Via Golgi, 19, I-20100 Milano (IT). **DELLA BIANCA,**  
**Serena [IT/IT];** Sealedair, Via Trento, 7, I-20017 Passirana  
di Rho (IT). **TOIA, Luca [IT/IT];** Via della Fontana, 14/A,  
I-21040 Carnago (IT).(74) Agents: **ADORNO, Silvano;** Società Italiana Brevetti  
S.p.A., Via Carducci, 8, I-20123 Milano et al. (IT).(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,  
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,  
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,  
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,  
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,  
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.(84) Designated States (regional): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian

[Continued on next page]

(54) Title: **HYDROGEN GETTER COMPOSITION**

(57) Abstract: The present invention relates to a composition capable of hydrogen sorption in a closed container at low pressure, comprising an unsaturated organic substance and a hydrogenation catalyst. Said unsaturated organic substance is a compound having general formula (A) or (A'), or a dimer or polymer thereof, or a copolymer wherein one of the structural units has the general formula (A) or (A'): wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are hydrogen or hydrocarbon moieties optionally comprising one or more heteroatoms, at least one among R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> being chosen in the group of alkenyl, alkynyl, arylalkenyl and arylalkynyl moieties, optionally comprising one or more heteroatoms.



patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

**Published:**

— *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

"HYDROGEN GETTER COMPOSITION"

The present invention relates to a composition capable of hydrogen sorption in a closed container at low pressure, and particularly it relates to a composition  
5 formed of an unsaturated organic substance and a hydrogenation catalyst.

Getter materials have been in use for a long time in all the industrial applications which require the vacuum maintenance in a closed system. A particularly important application uses the property of low thermal conductivity of the vacuum for realizing thermal insulation systems for any material or device.  
10 Said insulation is generally obtained by creating, outside the material or device to be insulated, a double wall with evacuated interspace.

Since hydrogen has, among gases, the largest thermal conductivity, it is particularly important to provide means for sorbing the traces of hydrogen which are still present in the evacuated interspaces so as to complete the achievement of  
15 vacuum. Furthermore, due to the small size of the hydrogen molecule, this gas outgases very easily from the walls of the evacuated containers and has to be continuously sorbed in order to maintain the thermal insulation property.

It is known that the organic compounds comprising unsaturated bonds among carbon atoms react with hydrogen in the presence of a suitable catalyst  
20 being converted into the corresponding saturated compounds. By virtue of this reactivity, said compounds, combined with a suitable catalyst, can be advantageously used as hydrogen getters.

Although in principle all compounds comprising a double or triple bond between two carbon atoms can sorb hydrogen, some fundamental requirements  
25 have to be satisfied for a compound to be industrially used. A first requirement relates to the specific rate of the reaction with hydrogen, which has to be high in order to avoid an accumulation of hydrogen in closed systems. Furthermore, it is necessary that said hydrogenation reaction be capable of occurring also at very low partial hydrogen pressures, in other words that the equilibrium of the reaction  
30 be shifted towards the products. Another requirement, important for ensuring that the unsaturated compound remains on the catalyst, is that said unsaturated

- 2 -

compound have a low vapor pressure within the whole range of working pressure and temperature.

Patent US 3,896,042 discloses a method for sorbing hydrogen from a closed system at low pressure and low temperature, which consists in placing inside said  
5 container a hydrogenation catalyst suitably supported on an inert substrate and coated with an unsaturated organic compound. The unsaturated organic compounds described in said patent are some arylacetylenes and particularly dimerized propargyl phenyl ether, dimerized benzylacetylene, dimerized phenylpropiolate, dimerized diphenyl propargyl ether and polydipropargyl ether  
10 of bisphenol-A.

Patent US 4,405,487 describes a combination of getter materials, which can be used for instance inside sealed containers for electronic and mechanical components, comprising a moisture getter and a hydrogen getter. The latter is formed of a hydrogenation catalyst and of a solid acetylenic hydrocarbon,  
15 comprising no nitrogen and sulphur heteroatoms. In fact, according to the patent teaching, these elements can bring about the generation of undesired by-products by hydrolysis. The acetylenic hydrocarbon which is indicated as particularly advantageous also from the point of view of the hydrogenation rate and of the hydrogen gettering capacity per gram of compound is 1,4-diphenylbutadiyne.

20 Patents US 5,624,598 and US 5,703,378 describe a composition for hydrogen sorption at low pressures and high temperatures, which can be used for instance for thermal insulation of the pipes for transportation of high temperature fluids. Said composition is formed of a suitable catalyst and of a hydrocarbon compound, or polymer, comprising triple bonds between carbon atoms and  
25 aromatic moieties selected among benzene, styrene, naphthalene, anthracene, diphenyl, fluorene, phenanthrene and pyrene. The presence of aromatic moieties has the purpose of raising the melting temperature of the unsaturated compounds and of their hydrogenated derivatives, so that they are solid at the working temperatures and pressures.

30 However, a first drawback of the compositions indicated in the last mentioned patents consists in that they are obtained as mixtures of many

compounds having different molecular weight. This involves problems in the control and reproducibility of the physical and chemical characteristics of the product. In particular, as it is known, it is difficult to obtain a solution of organic compounds having a very high molecular weight; consequently, the steps for the  
5 production of the final getter which require passing through a solution, such as the mixing with the hydrogenation catalyst and the deposition on a porous substrate, are difficult.

A second drawback of the above described composition for hydrogen sorption consists in the high production cost thereof. In facts, the synthesis of the  
10 unsaturated compounds or polymers is carried out by a condensation reaction starting from acetylenes and aromatic halides which requires the use of triphenylphosphine and palladium complexes as catalysts. At the end of the reaction, for economical reasons it is necessary to isolate the palladium complex, separating it from the reaction products so that it can be used again. Further, the  
15 other catalyst, triphenylphosphine, is a toxic product which should not be used in industrial processes in order to avoid safety and ecological problems.

Therefore, object of the present invention is providing a hydrogen getter composition free from said drawbacks. Said object is achieved by means of a hydrogen getter composition whose main features are specified in the first claim  
20 and other features are specified in the subsequent claims.

A first advantage of the hydrogen getter composition according to the present invention consists in that it allows final hydrogen pressures lower than those typical for getters according to the state of the art to be reached with particularly high sorption rates.

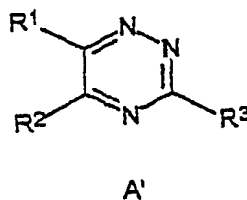
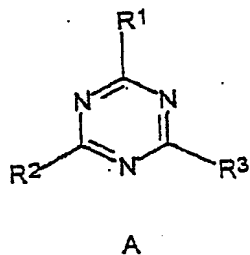
25 A second advantage of the hydrogen getter composition according to the present invention is that its production cost is very low. In fact, the synthesis of the unsaturated organic substances which are the components thereof is carried out from starting materials already available on the market and by means of processes which provide for high yields without using expensive catalysts and do  
30 not require subsequent separation steps.

These and other advantages of the hydrogen getter composition according to

the present invention will appear to those skilled in the art from the following detailed description of some embodiments with reference to the accompanying drawings, wherein:

- figure 1 is a scheme representing the measuring system used for evaluating the hydrogen sorption properties of the compositions according to the invention; and
- figure 2 is a graph showing the variation of the hydrogen sorption rate as a function of the sorbed hydrogen quantity per gram of unsaturated organic substance a of the getter composition according to the present invention.

The hydrogen getter according to the present invention comprises an unsaturated organic substance and a hydrogenation catalyst. The unsaturated organic substance can be a compound having general formula A or A':



20 wherein  $R^1$ ,  $R^2$  and  $R^3$  are hydrogen or hydrocarbon moieties optionally comprising one or more heteroatoms and wherein at least one among  $R^1$ ,  $R^2$  and  $R^3$  is selected in the group formed of alkenyl, alkynyl, arylalkenyl and arylalkynyl moieties, optionally comprising one or more heteroatoms.

25 Further, said unsaturated organic substance can be a dimer or a polymer of the compound of general formula A or A', as well as a copolymer wherein one of the structural units has the general formula A or A'.

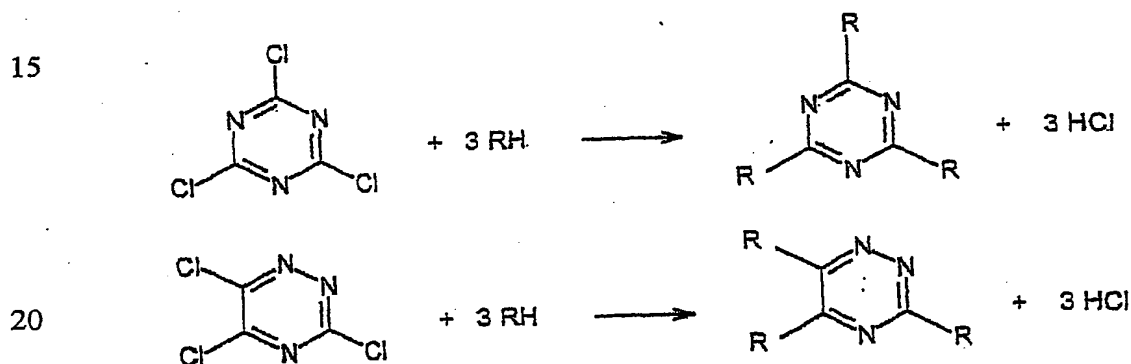
The three substituents  $R^1$ ,  $R^2$  and  $R^3$  can be all different from hydrogen and each one can have more than one unsaturated bond, so that the quantity of hydrogen irreversibly sorbed per gram of substance is maximized.

30 Furthermore, according to a particular embodiment of the present invention

the substituents  $R^1$ ,  $R^2$  and  $R^3$  comprise at least one heteroatom, selected among N, O and S and directly bound to the triazine ring. As a matter of fact it has been found that, contrary to the teachings of patent US 4,405,487, in some cases the presence of the heteroatoms does not affect the reactivity of the compound and the effectiveness of the hydrogenation catalyst. Preferred  $R^1$ ,  $R^2$  and  $R^3$  substituents are represented by the general formulae  $R-(C=C)_n-CH_2-O-$  and  $R-(C\equiv C)_n-CH_2-O-$ , wherein  $n \geq 1$  and R is any aliphatic or aromatic hydrocarbon moiety.

In order to allow a simplified synthesis of the unsaturated organic substance according to the present invention, in the case of a compound having general formula A or A', the three substituents  $R^1$ ,  $R^2$  and  $R^3$  are preferably the same.

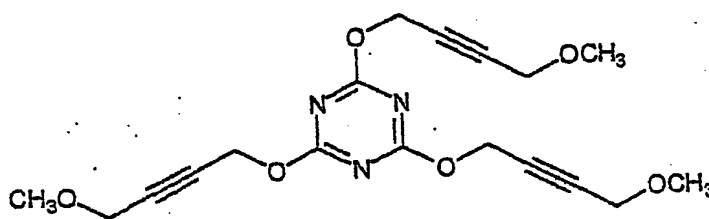
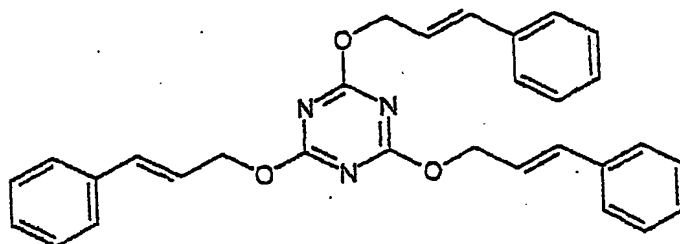
The compounds of general formula A or A' can be synthesized starting from the corresponding trichlorotriazine according to the following general scheme:



It is important to underline that the above described unsaturated organic substances can be used as the components of a hydrogen getter according to the present invention also in the liquid form, because they generally show good thermal resistance features. However, if the final application of the hydrogen getter involves particularly high working temperatures and solid unsaturated organic substances are required, very high melting points can be obtained by condensing two or more compounds having general formula A or A', so as to obtain dimers or polymers of said compounds. A further possibility consists in condensing two or more molecules of the compound having general formula A or

A' with any hydrocarbon compound.

Preferred for the use in the compositions of the invention are the two following organic compounds, both having general formula A:



Compound **a** is a new compound whose name, according to the IUPAC nomenclature, is 2,4,6-tris-(E-3-phenyl-prop-2-enyl-1-oxy)-1,3,5-triazine; this compound has molecular weight of 477,56 g/mol and its melting point has proved to be 128-129°C. This compound may be obtained, for instance, by reacting one equivalent of 2,4,6-trichloro-1,3,5-triazine with three equivalents of an alkaline metal cinnamate; this latter may be formed in-situ in the reaction medium.

Compound **b** has the IUPAC name 2,4,6-tris-(4-methoxy-but-2-ynyl-1-oxy)-1,3,5-triazine, and molecular weight of 375,38 g/mol.

The catalyst forming part of the getter composition according to the present invention can be any catalyst known in the art for hydrogenation reactions, such as transition metals belonging to Group VIII of the periodic table or salts or complexes thereof. Preferably, palladium supported on alumina or palladium on carbon are used.

Any known technique can be used for obtaining the getter composition according to the present invention. For example, it can be prepared mixing or



diluting the unsaturated organic substance in a suitable solvent and adding the hydrogenation catalyst to the obtained solution. After an accurate stirring of the mixture, the getter composition is obtained by evaporation of the solvent. In case of the use of palladium metal as the catalyst, this is preferably present in a quantity ranging between 0,1% and 10% by weight of the unsaturated organic substance.

In the following some examples relevant to the synthesis of organic compounds which can be advantageously used in the getter compositions of the invention, and to the measure of the hydrogen sorption properties of these compositions will be provided.

#### EXAMPLE 1

This example relates to the synthesis of compound a mentioned in the text.

50 g (0,36 mol) of cinnamic alcohol are dissolved in 180 ml of dry toluene. 20 g (0,36 mol) of KOH are added to the solution, and the resulting mixture is kept under stirring for one hour at room temperature. During this phase, potassium cinnamate is obtained. Then, a solution prepared starting from 18 g (0,10 mol) of 2,4,6-trichloro-s-triazine in 150 ml of toluene is added, allowing to react at room temperature for further 90 hours under stirring.

The reaction mixture is washed with water until pH is neutral. The solution is concentrated and the product is precipitated by addition of diisopropylether. The product is dried and analyzed by NMR and mass spectrometry, which prove it to be 2,4,6-tris-(E-3-phenyl-prop-2-enyl-1-oxy)-1,3,5-triazine. The compound has melting point of 128-129°C. 37 g of product are obtained, which are equal to a yield of about 78%.

#### EXAMPLE 2

The synthesis described in example 1 is repeated, but in this case 50 g (0,36 mol) of  $K_2CO_3$  are added to the initial mixture of cinnamic alcohol and KOH in toluene. 30 g of 2,4,6-tris-(E-phenyl-prop-2-enyl-1-oxy)-1,3,5-triazine are obtained, with a yield of about 64%.

#### EXAMPLE 3

This example relates to the synthesis of compound b mentioned in the text.

1,8 g (0,075 mol) of NaH are suspended in 20 ml of tetrahydrofurane (THF) under inert atmosphere. A solution containing 6 g (0,06 mol) of 4-methoxy-but-2-yn-1-ol in 20 ml of THF is added dropwise to the suspension, allowing the reaction to proceed for 3 hours at room temperature under stirring. Then, to this solution is added by slow dripping a solution containing 3,5 g (0,019 mol) of 2,4,6-trichloro-s-triazine in 30 ml of THF allowing to react for one night. The solvent is evaporated and the residue is first washed with 30 ml of water, and then acidificated with a 10% HCl solution. Three subsequent extractions with CH<sub>2</sub>Cl<sub>2</sub> and evaporation of the solvent are carried out. 6 g of a deep yellow oil are obtained. The product is purified by chromatography on a silica column, using ethyl acetate as eluent. At the end 4,3 g of a yellow liquid are obtained, with a yield of 60%. The final compound is liquid, but it can be impregnated on palladium on carbon obtaining a composition suitable for the purpose of the invention, which has a null vapor pressure in the hydrogen sorption test.

15

#### EXAMPLE 4

This example relates to the measure of the hydrogen sorption capacity of a composition according to the invention containing compound a.

For this measure the system diagrammatically shown in figure 1 is used, formed of a hydrogen reservoir 10, connected by means of a needle valve 11 to a chamber 12 having known volume, whose pressure is measured by means of a capacitive manometer 13; chamber 12 is connected by means of valve 14 to a pumping system (not shown in the figure). Furthermore, chamber 12 is connected, by means of a liquid nitrogen trap 15 and a valve 16, to measuring chamber 17; this latter chamber is connected in turn to a pumping system (not shown in the figure) by means of valve 18. Trap 15 has the purpose of blocking the passage of possible impurities from chamber 12 to chamber 17.

10 g of compound a prepared as described in example 1 are dissolved in 50 ml of ethyl alcohol. 10 g of 5% palladium on carbon of the company Aldrich are added to the solution; this material consists in carbon powder having a high specific surface on which palladium in metal form has been deposited in a quantity of 5% by weight of the sum of carbon and Pd. The obtained solution is

stirred for half an hour, and subsequently the solvent is eliminated by evaporation, thus obtaining a residue formed of a mixture of compound a and palladium on carbon.

1 g of the mixture is introduced, in the powder form, in measuring chamber  
5 17. Chamber 17 is evacuated to a pressure of  $1,33 \times 10^{-3}$  mbar, then the chamber is isolated from the pumping by closing valve 18. With valve 16 closed, valve 11 is opened until the pressure in the system has reached the value of 6,7 mbar. Now, valve 16 is opened and valve 11 is closed, while the pressure decrease in the system due to the sorption by the sample under analysis is measured. When the  
10 pressure is decreased to one tenth of the initial value (0,67 mbar) the procedure for the hydrogen dosage is repeated. The same procedure is repeated until when, after the introduction of hydrogen in the measuring chamber, no sorption by the sample is detected. The pressure values as a function of the testing time are processed, thus obtaining sorption rate values (S) as a function of the sorbed hydrogen  
15 quantity (Q) by means of the following formulae:

$$Q_i = (P_0 - P_i) \times V$$

$$S_i = - V/P_i \times (dP/dt)$$

wherein  $Q_i$  is the quantity of hydrogen sorbed at time i,  $S_i$  the volumetric  
sorption rate at time i,  $P_0$  the initial pressure,  $P_i$  the pressure at time i, V the total  
20 volume of the measuring system.

Q and S are then normalized with respect to the weight of the getter sample. The results of the test are given in figure 2. As it can be seen from the figure, the composition containing compound a sorbs a total quantity of about 67 (mbar x l/g) of hydrogen, equivalent to about 133 (mbar x l/g) if referred to compound a alone;  
25 the sorption rate varies from an initial value of about  $5,3 \times 10^{-3}$  (mbar x l/g x s) to a value of about  $2,7 \times 10^{-5}$  (mbar x l/g x s) when the sorption capacity of the composition is almost exhausted.

#### EXAMPLE 5

The test of example 4 is repeated on a sample of one gram of composition of  
30 the invention, obtained impregnating 0,5 g of compound b produced as described in example 3 on 0,5 g of 5% palladium on carbon. This composition shows a

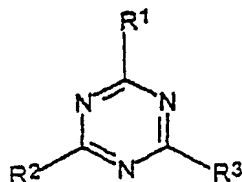
- 10 -

hydrogen sorption capacity of 186 (mbar x l/g) if referred to compound b alone, with sorption speed equal to  $2,7 \times 10^{-3}$  (mbar x l/g x s) at the beginning of the test and  $8 \times 10^{-6}$  (mbar x l/g x s) at the end thereof.

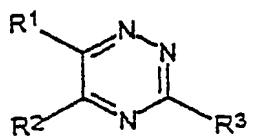
Possible variations and additions can be made by those which are skilled in the art to the hereby described and illustrated embodiment remaining within the scope of the invention itself.

## CLAIMS

1. A hydrogen getter composition comprising an unsaturated organic substance and a hydrogenation catalyst, characterized in that the unsaturated organic substance is a compound having general formula A or A', a dimer or polymer thereof, or a copolymer wherein one of the structural units has the general formula A or A':



A

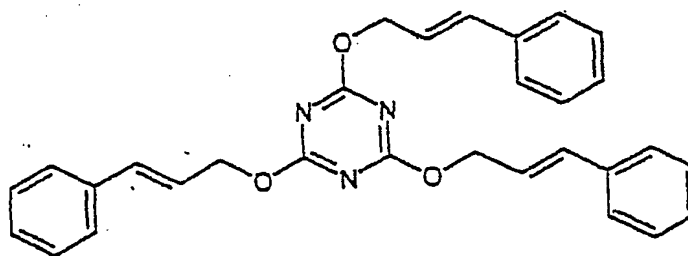


A'

- wherein  $R^1$ ,  $R^2$  and  $R^3$  are hydrogen or hydrocarbon moieties optionally comprising one or more heteroatoms, at least one among  $R^1$ ,  $R^2$  and  $R^3$  being selected in the group of alkenyl, alkynyl, arylalkenyl and arylalkynyl moieties, optionally comprising one or more heteroatoms.
2. A hydrogen getter composition according to claim 1, characterized in that  $R^1$ ,  $R^2$  and  $R^3$  comprise at least one heteroatom selected in the group of N, O and S, which is directly bound to the triazine ring.
  3. A hydrogen getter composition according to claims 1 or 2, characterized in that the unsaturated organic substance has the general formula A or A' and that  $R^1$ ,  $R^2$  and  $R^3$  are the same.
  4. A hydrogen getter composition according to the preceding claim, characterized in that  $R^1$ ,  $R^2$  and  $R^3$  can be represented by the general formula  $R-(C=C)_n-CH_2-O-$ , wherein  $n \geq 1$  and R is any aliphatic or aromatic hydrocarbon moiety.
  5. A hydrogen getter composition according to claim 3, characterized in that  $R^1$ ,  $R^2$  and  $R^3$  can be represented by the general formula  $R-(C \equiv C)_n-CH_2-O-$ , wherein  $n \geq 1$  and R is any aliphatic or aromatic hydrocarbon moiety.
  6. A hydrogen getter composition according to one of the preceding claims, characterized in that the hydrogenation catalyst is selected among the metals of Group VIII of the periodic table, salts and complexes thereof.
  7. A hydrogen getter composition according to the preceding claim, characterized in

that the hydrogenation catalyst is Pd supported on alumina or carbon.

8. A hydrogen getter composition according to the preceding claim, characterized in that the quantity of palladium is between 0,1% and 10% by weight of the unsaturated organic substance.
9. An unsaturated organic substance having formula:



10. A process for the synthesis of the organic substance according to the preceding claim, characterized in that 2,4,6-trichloro-1,3,5-triazine is reacted with three equivalents of an alkaline metal cinnamate.

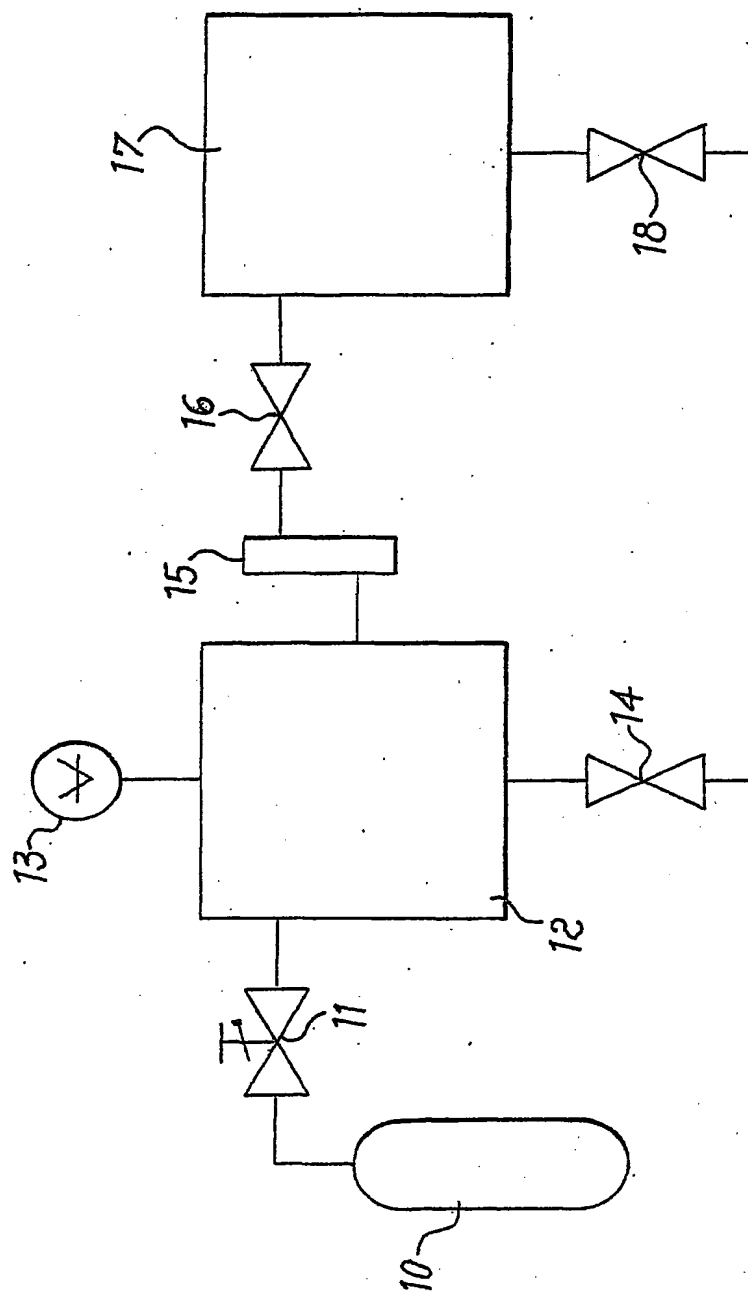
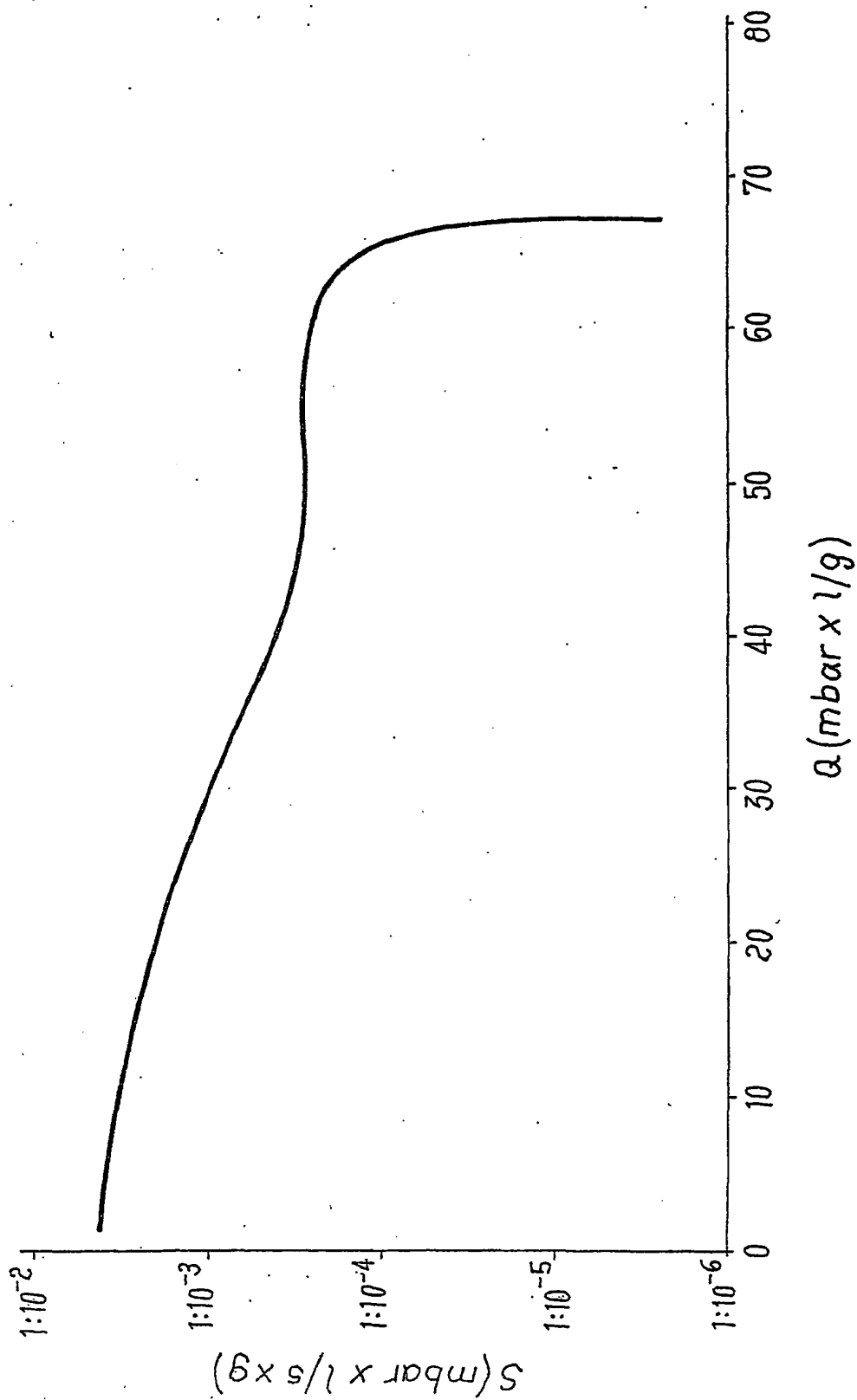
Fig. 1

Fig. 2



## INTERNATIONAL SEARCH REPORT

onal Application No

PCT IT 01/00105

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C01B3/00 C07D253/06 C07D251/30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 C01B C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 624 598 A (PHILLIP BRADLEY L ET AL) 29 April 1997 (1997-04-29) cited in the application the whole document	1
A	US 5 703 378 A (PHILLIP BRADLEY L ET AL) 30 December 1997 (1997-12-30) cited in the application the whole document	1
A	US 4 616 014 A (TERAJI TSUTOMU ET AL) 7 October 1986 (1986-10-07) example 16	1
A	WO 99 63298 A (MARCONI AEROSPACE DEFENSE SYST) 9 December 1999 (1999-12-09) the whole document	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the International filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the International filing date but later than the priority date claimed

\*T\* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\* & \* document member of the same patent family

Date of the actual completion of the international search

1 August 2001

Date of mailing of the International search report

09/08/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Puetz, C

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

/IT 01/00105

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5624598	A	29-04-1997	US 5703378	A	30-12-1997
US 5703378	A	30-12-1997	US 5624598	A	29-04-1997
US 4616014	A	07-10-1986	AU 8926982	A	28-04-1983
			DE 3276164	D	04-06-1987
			DK 453882	A	23-04-1983
			EP 0077983	A	04-05-1983
			ES 516724	D	16-11-1983
			ES 8401042	A	16-02-1984
			ES 523299	D	16-04-1985
			ES 8601934	A	01-03-1986
			ES 523300	D	01-10-1984
			ES 8500247	A	01-01-1985
			FI 823544	A	23-04-1983
			GR 76714	A	29-08-1984
			JP 58099468	A	13-06-1983
			NO 823506	A	25-04-1983
			OA 7236	A	30-04-1984
			ZA 8207310	A	31-08-1983
WO 9963298	A	09-12-1999	AU 4420699	A	20-12-1999